

# Characterization of soy protein/styrene–butadiene rubber composites<sup>☆</sup>

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Received 19 March 2004; revised 6 July 2004; accepted 6 July 2004

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## Abstract

The use of renewable soy protein aggregates as a reinforcement network in Styrene–butadiene rubber composites is investigated by dynamic mechanical method. The rigid nature of dry protein has a high shear elastic modulus of  $\sim 2$  GPa and therefore is suitable as a reinforcement phase in rubber composites. The addition of soy protein to the rubber composites generates a significant reinforcement effect. The characterization includes the dynamic mechanical and FTIR studies of the annealing effect on the composite modulus. The increasing elastic modulus with time in the constant temperature experiments indicates the hardening of protein through a mechanism of dehydration and structure change. This is also accompanied by an increase in protein density. The apparent rate of modulus increase during annealing at different elevated temperatures up to 140 °C does not show significant differences. A comparison is also made with rubber composites prepared from an aqueous dispersion of carbon black. The result indicates dry protein composites have higher shear elastic moduli at the same weight fractions of filler.

Published by Elsevier Ltd.

**Keywords:** A. Particle-reinforcement; B. Mechanical properties; Soy protein

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## 1. Introduction

In recent years, many investigations have been made on the modulus enhancement of rubbers by natural materials. Only a few examples are given here [1–3]. From the viewpoint of renewable materials and environmental reasons, soy protein has been investigated as a component in plastic and adhesive composites [4–8], but has been rarely investigated as a reinforcement component in rubber composites. Dry soy protein is a rigid material and has a shear elastic modulus of  $\sim 2$  GPa under ambient conditions [5]. Because the high rigidity in reinforcement phase is one of the requirements in rubber reinforcement, dry protein is therefore a possible candidate for rubber reinforcement. The attempt to use protein in rubber latex can be traced back to 1930's. A few patents [9–11] had claimed the use of protein

in rubber composites. For example, Lehmann and coworkers had demonstrated the use of casein, a milk protein, in natural rubber latex to achieve approximately four times increase in the modulus [11]. In rubber reinforcement, the factors such as aggregate structure, effective filler volume fraction, and elastic modulus of filler clusters have important impact on the modulus of rubber composites [12].

In this study, the rubber matrix chosen is a styrene–butadiene rubber with a small amount of carboxylic acid containing monomer units because previous studies have indicated the importance of interaction between filler and matrix [13]. Soy protein contains a significant amount of carboxylic acid and substituted amine group [14]. Ionic interaction between protein and rubber matrix is therefore possible. Structurally, Soy protein is a globule protein and its aggregate is similar to colloidal aggregates. For practical applications, the issue of moisture sensitivity in some applications is always associated with natural materials, but it may be improved through product formulation and/or selective applications. For example, it may be used as a component in multi-layered structures, in coated objects, in elevated temperature applications or as a rubber part in

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<sup>☆</sup> Names are necessary to factually report on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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greasy/oily environments where the moisture effect is minimum. The aim of this research is to obtain the information of heat treatment on soy protein aggregates and the degree of reinforcement soy protein aggregates can contribute in rubber composites.

The composite system investigated here is a simpler system prepared by casting from only two components, soy protein dispersion and carboxylated styrene–butadiene latex. The system is less complicated than the high temperature compounded filled rubbers, which usually involve many ingredients and high temperature shear actions. With few variables, a more clear understanding is therefore, possible. To give some background on the rubber matrix of this composite, the properties of carboxylated SBR will be described briefly. Carboxylated SBR is classified as an ion-containing polymer where the viscoelastic properties are affected by the molecular weight, the degree of crosslinking, the glass transition temperature ( $T_g$ ), the copolymer composition, the number of ionic functional groups, the size of ionic aggregation, the degree of neutralization, and the size of the neutralizing ions [15, 16]. Previous studies also have shown honeycomb-like structures in the film of carboxylated latexes due to a higher concentration of carboxylic acid groups on the particle surface [17]. Mechanically, the elastic modulus of base rubber is not significant when compared with the modulus of filler network in highly filled elastomeric composites [13].

## 2. Experimental procedures

### 2.1. Starting materials and composite preparation

The soy protein isolate used in this research is a slightly enzyme hydrolyzed soy protein isolate (PRO-FAM 781, Archer Daniels Midland Company, Decatur, IL). It contains more than 90% protein, ~6% ash and ~4% fat. Sodium hydroxide, used to adjust pH, is ACS grade. The carboxylated styrene–butadiene (SB) latex is a random copolymer of styrene, butadiene, and a small amount of carboxylic acid containing monomers (CP 620NA, Dow Chemical Company, Midland, MI.). The glass transition temperature of carboxylated SB Latex is ~10 °C determined by differential scanning calorimetry (DSC). The styrene/butadiene ratio estimated from the glass transition temperatures of a series of commercially available carboxylated styrene butadiene is approximately 65/35. The dried latex is not known to be soluble in any solvent. Therefore, the molecular weight was not measured and it had no consequence in this study. The latex received has ~50% solids and a pH of ~6. The particle size of latex is ~0.18  $\mu\text{m}$ .

The soy protein isolate was first dispersed in water and the pH of the dispersion was adjusted to 9 with sodium hydroxide. The alkaline soy protein dispersion was then cooked under stirring at 55 °C for 60 min to help with

the dispersion of the soy protein. After cooking, the cloudy soy protein dispersion was then mixed with SB latex and the pH of mixture was adjusted to 9. The final aqueous dispersion has 25% solids and 75% water. The composite of soy protein isolate and carboxylated SB latex was prepared by first casting the mixture onto an aluminum mold covered with Teflon released sheet (BYTAC from Saint-Gobain Performance Plastics) and then allowing it to dry at 75 °C for 2–3 days.

### 2.2. Annealing experiment

To determine an appropriate condition for the preparation of protein/rubber composites, annealing experiments by dynamic mechanical method were conducted on 20/80 Soy/SB Composites. The 20/80 composition is soft enough to have good adhesion on the parallel plate for kinetic measurements. A parallel plate instead of torsion rectangular geometry is used here because it allows the rapid mounting of samples after the setup is conditioned at a certain temperature and it allows the automatic adjustment of thickness changes due to dehydration. For these experiments, composites were dried at 75 °C for 2 days. The films with thickness of 0.8–1.5 mm were prepared. Dried carboxylated SBR film contains 1% moisture and the dried 20/80 Soy/SB composite has a moisture content of 3.5% as measured by a halogen moisture analyzer (Mettler Toledo HR73) at 105 °C for 60 min. For all isothermal annealing experiments, the storage modulus,  $G'(\omega)$ , was measured using Rheometric ARES with 8 mm parallel plate geometry. The fixture was first conditioned at a desired temperature for 15 min and then a 8 mm disk sample with a thickness of 0.8–1.5 mm was inserted between the top and bottom plates. In order to assure no slippage between the sample and plates at the end of annealing experiments, a small normal force of about 500 g was applied onto the sample. The measurement was conducted in the linear viscoelastic region with a frequency of 0.16 Hz (1 rad/s) and 0.05% strain. The linear viscoelastic region was determined by a strain sweep experiment at 1 rad/s from  $10^{-3}$  to  $10^2\%$  strain in the temperature range from 80 to 180 °C.

To examine if there is structure changes due to the effect of annealing, transmission spectra in the midrange Infrared region were obtained using a Nicolet Impact 410 Fourier Transform Infrared Spectrometer (FTIR). The spectra were analyzed using Nicolet's Omnic software. For FTIR studies, both 20/80 and 40/60 Soy/SB composites were measured.

### 2.3. Shear elastic modulus measurement

For elastic modulus measurements, composites containing 10 to 40% by weight of soy protein isolate were prepared. They were dried at 75 °C for 3 days, removed from the mold, and annealed at 110 and 140 °C for 24 h, respectively. The film of 100% carboxylated SB rubber was prepared by adjusting the pH of latex to 9 and dried under

the same conditions as that of the Soy/SB composites. The films, with a thickness of 2.5–3 mm, were stored in sealed plastic bags under ambient conditions. There was no significant change in the moisture content of the samples during the storage because SB rubber is hydrophobic and can significantly reduce the moisture sensitivity of protein composites. The dried carboxylated SBR film contains less than 0.3% moisture and the dried Soy/SB composites have moisture contents less than 0.8%. Carbon black composites were prepared in the same way as that of protein by mixing an aqueous dispersion of carbon black and styrene–butadiene latex. Aqueous dispersion of carbon black N-339 (Sid Richardson, Fort Worth, TX) was prepared by dispersing carbon black in water with the aid of a surfactant, sodium lignosulfonate (Vanisperse CB, Lignotech USA, Rothschild, WI). The weight fraction of surfactant based on carbon black is 3%. The dispersion was homogenized at 10,000 rpm for 1 h.

The weight fractions of soy protein in the composites were converted to volume fractions by measuring the density of soy protein and that of SBR samples using a low viscosity poly(dimethylsiloxane) as an immersion liquid. The agreement between the sum of component volumes and the measured composite volume is  $\pm 2\%$ . The same procedure was used to determine the density and volume of carbon black and its composites.

Time sweep and temperature ramp experiments were conducted using torsion rectangular geometry. Torsional bars with an approximate dimension of  $40 \times 12 \times 3$  mm were mounted onto a torsion rectangular fixture and dynamic mechanical measurements were conducted at a frequency of 0.16 Hz (1 rad/s) and a strain of 0.05%.

The elastic modulus at linear region was obtained by a time sweep experiment at 140 °C, 0.16 Hz (1 rad/s), and 0.05% strain. From the previous annealing experiments, it is known that the annealing in oven is completed in 24 h at 140 °C. However, all annealed samples are checked by the time sweep experiments for 30–60 min and the average value at equilibrium (less than 1% increase in 30 min) was taken as the elastic modulus. Three to seven specimens were measured for each soy protein or carbon black composition and the average value was taken for each composition (Fig. 5).

### 3. Results and discussions

#### 3.1. Effect of temperature treatment

Water is a plasticizer for soy protein. To obtain a rigid protein, high temperature treatment is necessary. Fig. 1 shows the increase in the elastic moduli of 20/80 Soy/SB composites at 110 °C. When the annealed sample was re-hydrated with different amount of water, it was found the dehydration curve is different from the initial annealing curve. The amount of moisture shown in Fig. 1 was

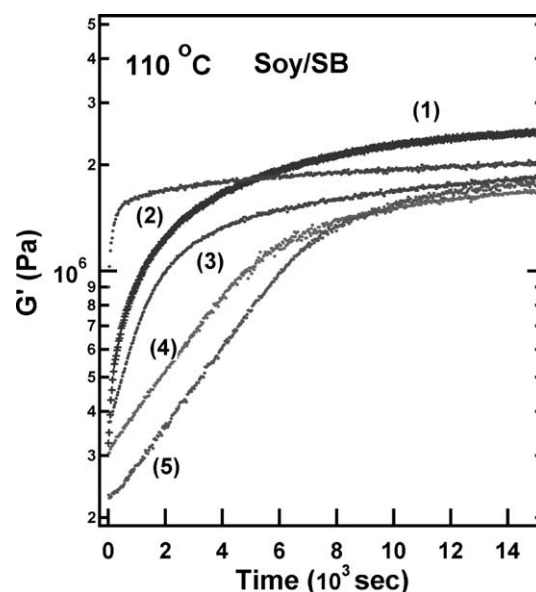


Fig. 1. 20/80 Soy/SB composites. Curves from top to bottom: (1) annealing at 110 °C (2) dehydration at 110 °C with added moisture content of 1.6% (3) dehydration at 110 °C with added moisture content of 3% (4) dehydration at 110 °C with added moisture content of 5.6% (5) dehydration at 110 °C with added moisture content of 10%.

determined by weight gain after an annealed composite was immersed in water for a certain period, removed and equilibrated. For clarity, only 4.2 h of annealing and dehydration curves are shown in Fig. 1. Dehydration curves only approach equilibrium after  $\sim 20$  h at 110 °C. The characteristics of the dehydration curves are a linear initial rate and the slow approach to equilibrium at longer time. On the other hand, the annealing curve has a higher rate at a comparable amount of moisture and reaches equilibrium in a shorter time. To examine if the protein structure has changed due to the high temperature treatment, FTIR spectra were obtained for the protein, SB rubber, and 40/60 composite before and after annealing at 140 °C (Fig. 2). Because the change in spectra due to the annealing effect comes mostly from the structure change of the soy protein, the composite with a high protein fraction (40%) is used to more clearly demonstrate the effect. 20/80 Soy/SB composite annealed at 110 °C showed the same effect. The structure change of composite (Fig. 2 (b)) is mostly from the change in protein amide-I ( $1650\text{ cm}^{-1}$ ) and amide-II ( $1540\text{ cm}^{-1}$ ) bands (Fig. 2(a)). The intensity difference shown in Fig. 2(b) is based on the normalization of the spectra with the strong aromatic (styrene) absorbance peak at  $700\text{ cm}^{-1}$ , which does not change upon the annealing. Alternatively, the absorbance peak at  $910\text{ cm}^{-1}$  (Fig. 2(b) and (c)) also does not vary with the annealing condition and can be used as an internal standard. The reduction of amide bands is most likely due to the continuing hydrolysis of amide bonds under the alkali and high temperature condition. The alkali hydrolysis of amide bond produces primary amine (N–H bending at  $1650\text{--}1580\text{ cm}^{-1}$ ) and carboxylate ion (C=O stretching at  $1600\text{--}1590\text{ cm}^{-1}$ ).

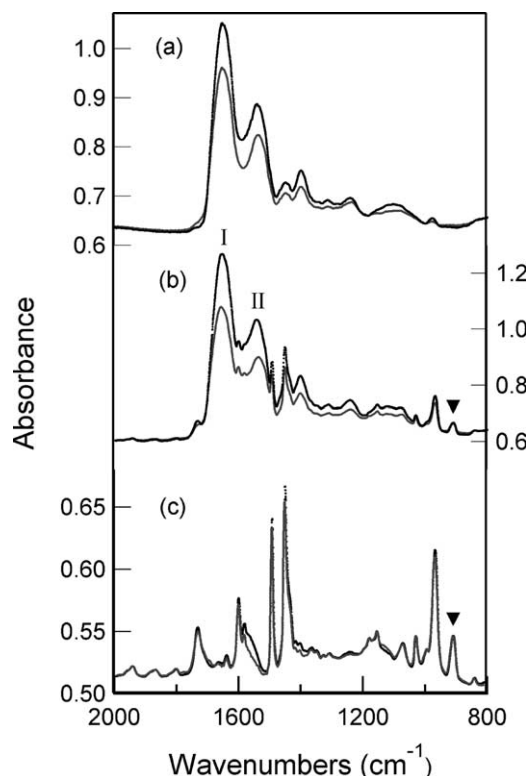


Fig. 2. FTIR spectra of soy protein, SB, and 40/60 Soy/SB composite before and after annealing at 140 °C. (a) Soy protein spectra show a significant reduction in amide-I and II bands after the annealing, (b) 40/60 Soy/SB composite spectra show a significant reduction in amide-I and II bands after the annealing, (c) SB spectra show only minor changes after the annealing. Absorbance peak at 910  $\text{cm}^{-1}$  used for intensity normalization is indicated by ▼.

These absorbance bands are buried under the amide I and II bands. This is a simplified explanation because the actual structure rearrangement is likely to be more complex due to the complicate structure of soy protein. A detailed study of such molecular rearrangements is however, beyond the scope of this investigation. The dehydration and structural changes also cause an observable increase of 0.1  $\text{g}/\text{cm}^3$  in protein density.

To obtain the information of time required to anneal the composites, isothermal experiments were conducted from 110 to 180 °C. The results are shown in Fig. 3. The moduli increase at 160 and 180 °C have contributions from the SB rubber, likely through the oxidative crosslinking of butadiene units. From these experiments, the upper temperature limit of annealing for this composite is 140 °C. To obtain information on the apparent rate of annealing, an empirical model was used. The purpose of empirical fitting of annealing data is to enable the differentiation of these curves since they are visually similar. The model used is not unique. Other empirical models such as that by Kamal et al. [18] can also serve this purpose as well. The equation used here is  $\alpha = 1 - \{(n-1)k(t-t_0) + 1\}^{(1/1-n)}$ , which was originally derived from an  $n$ th order reaction with equal concentration of

reactants [19]. The extent of rate change,  $\alpha$ , can be expressed in terms of elastic modulus,  $G'$ , that is proportional to the extent of dehydration/structural changes.  $\alpha$  is equal to  $(G'_t - G'_0)/(G'_\infty - G'_0)$ , where  $G'_\infty$  is equal to  $G'$  at equilibrium,  $G'_0$  is  $G'$  in the beginning of measurement, and  $G'_t$  is  $G'$  at time  $t$  between the start and the end of measurement. The fitting parameters are summarized in Table 1 and are given as coefficient values  $\pm 99.73\%$  confidence interval by Igor Pro software. Compared the annealing rates in the range between 110 and 140 °C, only small differences are observed. This may indicate SB phase plays a control role in the diffusion of moisture. It is also observed that above  $\sim 140$  °C, significant heat hardening occurs in SBR and the fitting parameters, both  $n$  and  $k$ , start to deviate greatly from the fitting parameters in the temperature range of 110 to 140 °C. This can also be observed from the 100% SB annealing curve at 160 °C (Fig. 3), where the elastic modulus does not reach equilibrium within the same annealing period as that in the case of 120 and 140 °C. The empirical fitting that works well in the case of 120 and 140 °C does not fit the entire annealing curve any more, but only the first  $\sim 15,000$  s. Such behavior becomes quite significant at 180 °C.

### 3.2. Dynamic shear modulus of protein composites

To determine the shear elastic modulus, all samples were annealed at 140 °C before the measurement. The temperature ramp data is shown in Fig. 4. Annealed soy protein is glass like in the temperature range measured ( $-40$  to 140 °C). Its elastic modulus is similar to that of rubber phase below the glass transition temperature. Such rigidity explains its ability to reinforce the rubber in the rubber plateau region. As expected in this type of composites, the peak positions in the loss modulus are not affected by the presence of different amounts of filler.  $\tan\delta$  maximum decreases and shifts systematically to a lower temperature as the filler content is increased. This behavior was also observed in SBR reinforced by polymeric fillers [20,21]. Vieweg and coworkers [21] have studied this transition zone and indicated the fillers affect the polymer molecular motions with mode lengths of an order of several nanometers.

### 3.3. Comparison with carbon black filled composites

To obtain the information on the ability of dry soy protein to reinforce rubber composites, it is a common practice to compare the filler with well-known carbon black. The comparison of elastic modulus vs. weight fraction of filler is presented in Fig. 5(a) and the elastic modulus vs. volume fraction is presented in Fig. 5(b). It is observed that dry soy protein composites yield higher elastic moduli at the same weight fractions of filler. However, carbon black has a higher density (1.73  $\text{g}/\text{cm}^3$ ) than that of dry protein (1.30  $\text{g}/\text{cm}^3$ ). Therefore,



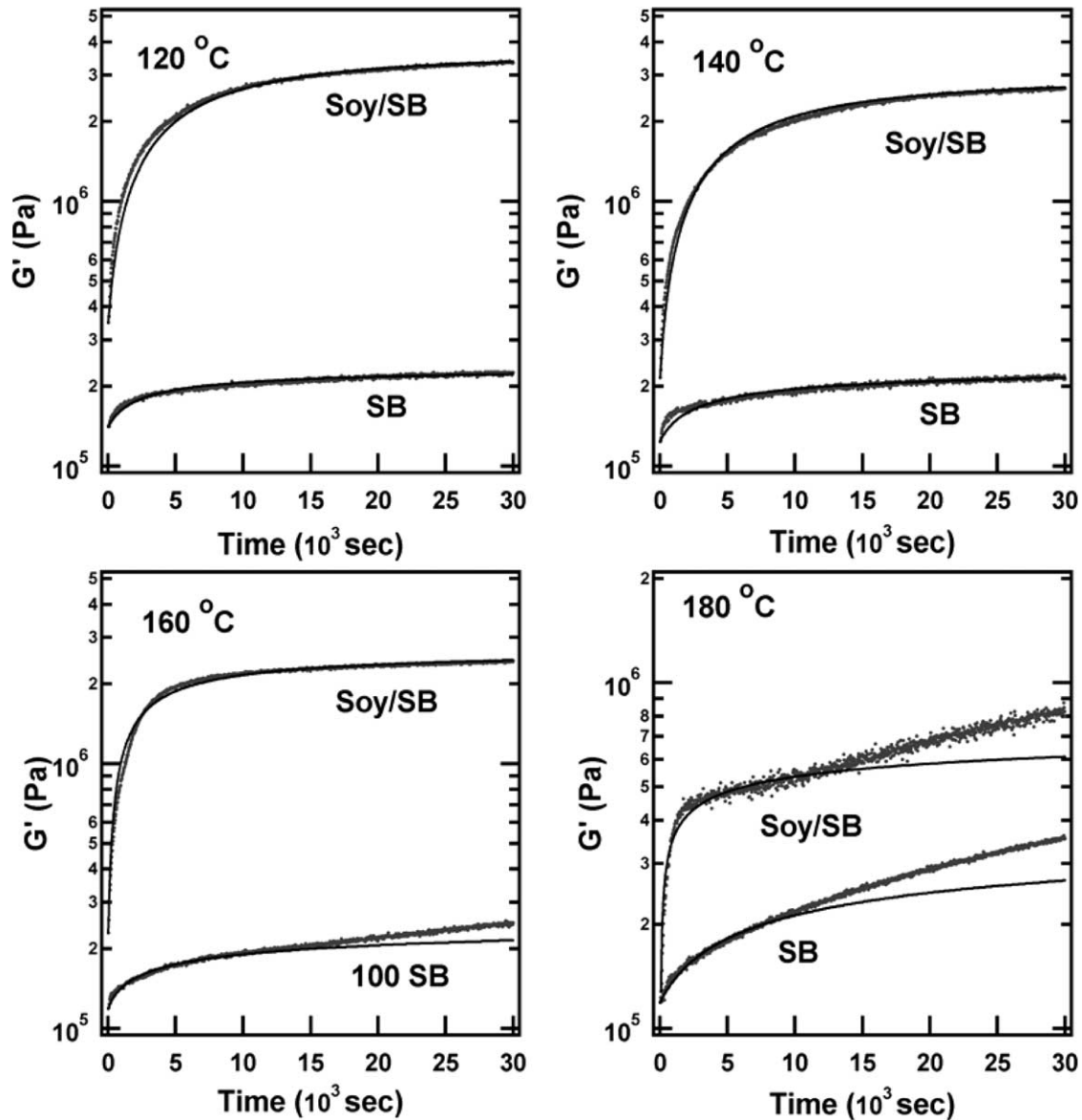


Fig. 3. Isothermal annealing at 120, 140, 160 and 180 °C. The points are experimental data. The lines represent the fitting of an empirical kinetic model.

the elastic moduli of protein composites are only slightly higher than that of carbon black at the same volume fractions of filler. The result is obviously interesting because the primary particle size of protein cluster is much greater than that of carbon black. Previously in our laboratory, the average primary particle size of dry protein clusters was determined to be  $\sim 330$  nm and the fractal dimension was measured to be 1.34. [22] An example of protein clusters is shown in Fig. 6. To understand a little more about this case, theoretical models can more or less help to clarify the situation. The recent theoretical developments on the reinforcement mechanism of particle aggregates as reviewed by Heinrich and Kluppel [12] have shown some promise and certain quantitative comparison between theory and experiment has been demonstrated. One of theories on

the particle-reinforced elastomer is cluster–cluster aggregation model (CCA) [23–25] that relates the fractal structure of particle aggregate to the dynamic elastic modulus. This model can describe the reinforcement

Table 1  
Kinetic Parameters of Soy/SB Composites

Temp.(°C)	$n$	$k \text{ (ss}^{-1}) \times 10^4$
110	$1.46 \pm 0.01$	$2.34 \pm 0.02$
120	$1.55 \pm 0.01$	$1.81 \pm 0.02$
130	$1.63 \pm 0.01$	$2.54 \pm 0.03$
140	$1.52 \pm 0.01$	$1.52 \pm 0.01$
160 <sup>a</sup>	$2.58 \pm 0.04$	$5.2 \pm 0.2$
180 <sup>a</sup>	$15.2 \pm 0.8$	$8.2 \pm 1.4$

<sup>a</sup> Only fit to the period from the beginning of the annealing to the divergent point of the experimental data and fitting curve in Fig. 3.

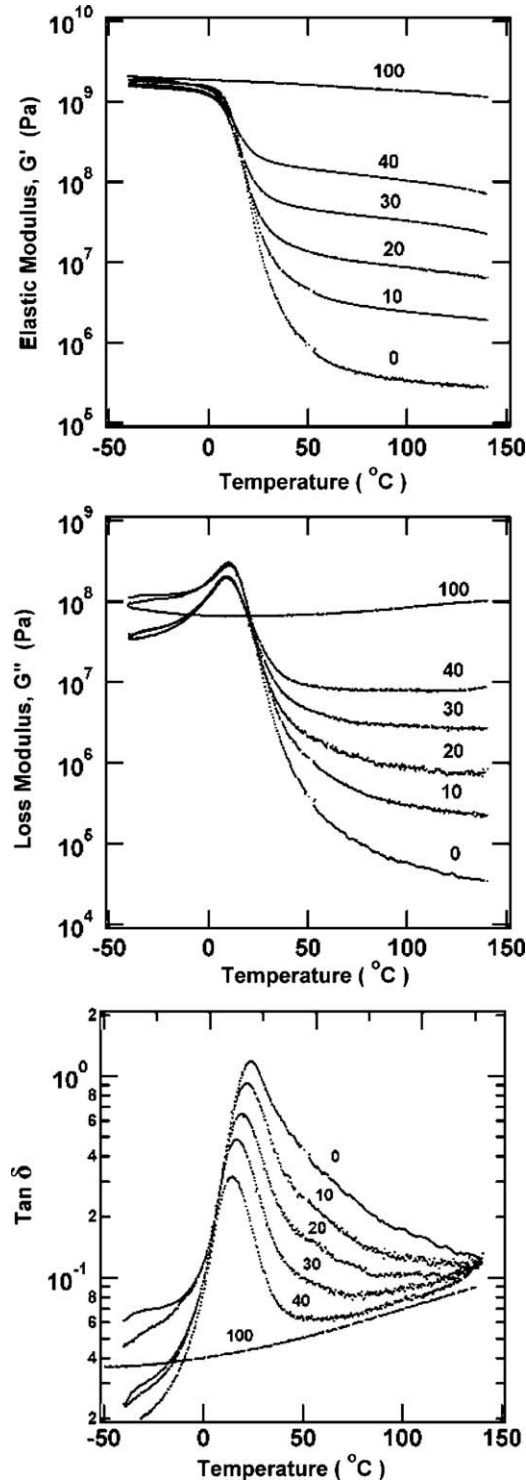


Fig. 4. Temperature ramp experiments of the soy protein, Soy/SB composites, and SB rubber. The number on the top of each curve indicates the wt % of soy protein in the Soy/SB composites.

mechanism above a percolation threshold. The model description on the reinforcement effect of some carbon black and polymeric fillers has been shown to be reasonable [12]. For the convenience of explanation,

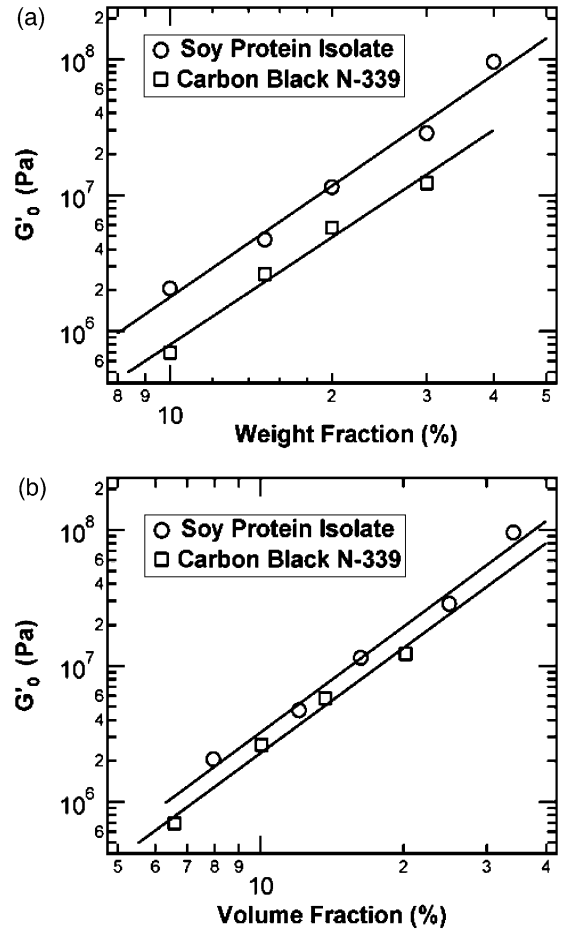


Fig. 5. Shear elastic moduli measured at 140 °C: (a) annealed Soy/SB and carbon black/SB composites at different weight fractions, (b) same composites at different volume fractions.

the equation is shown below.

$$G \cong G_p \phi^{(3+d_{f,B})/(3-d_f)} \quad \text{for } \phi > \phi^* \quad (1)$$

Where  $G$  is identified as small strain storage modulus  $G'_0$  in the dynamic mechanical measurement of rubbery materials.  $G_p$  is the averaged elastic bending-twisting modulus of different kinds of angular deformation of the cluster units, i.e., filler particles or bonds between filler particles.  $\phi$  is the effective filler volume fraction,  $d_{f,b} \approx 1.3$  is the fractal dimension of the CCA-cluster backbone, and  $d_f$  is the fractal dimension of the cluster. For typical CCA-clusters with  $d_f \approx 1.8$ , Eq. (1) predicts the exponent  $(3+d_{f,B})/(3-d_f) \approx 3.5$ .

Based on CCA model, a smaller particle size in aggregates gives a greater effective volume fraction and a lower fractal dimension of clusters gives a lower exponent on the effective volume fraction. For protein clusters, the primary particle size of  $\sim 330$  nm is larger than that of carbon black N339 ( $\sim 50$  nm). The effective volume fraction of protein cluster is therefore smaller. In this case, the exponent of  $\sim 2.6$  is similar for both carbon black and protein composites as shown in Fig. 5(b). The factor

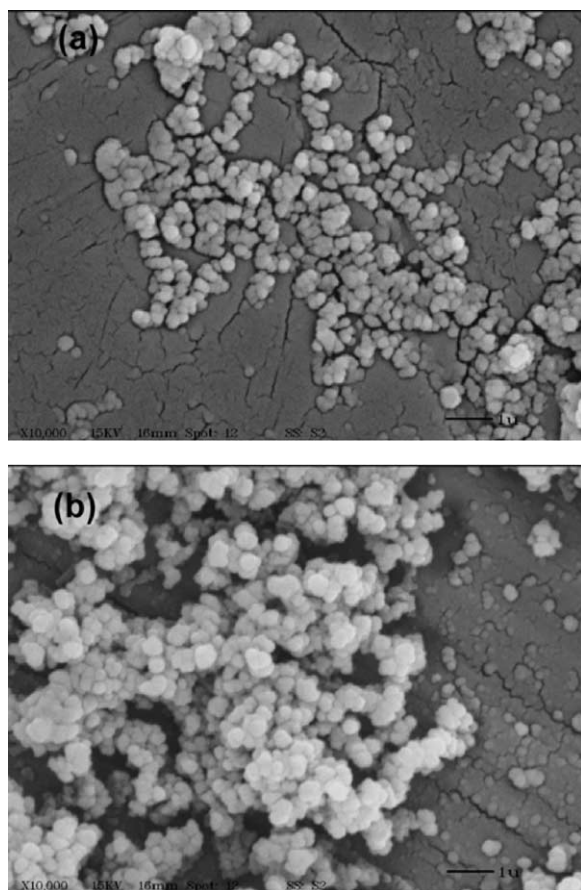


Fig. 6. (a) Soy protein clusters at a lower concentration region on an aluminum stage. (b) Soy protein clusters at a higher concentration region on the same aluminum stage. The scale of black bar located at the right bottom corner of the pictures is 1  $\mu\text{m}$ .

$\phi^{(3+d_{f,B})/(3-d_f)}$  is therefore larger for carbon black composites. The fact composite modulus of dry protein is higher than that of carbon black indicates bonds between protein particles (factor  $G_p$ ) is stronger than that of carbon black due to the ionic interactions between protein particles.

#### 4. Conclusions

Soy protein clusters when annealed at 140 °C exhibited high rigidity suitable for rubber reinforcement. The characterization includes the dynamic mechanical and FTIR studies of the annealing effect on the composite modulus. The increasing elastic modulus with time in the constant temperature experiments indicates the hardening of protein through a mechanism of dehydration and structure change. FTIR studies indicate the reduction of amide-I and amide-II bands in the annealed protein. This is also accompanied by an increase in protein density. The apparent rate of modulus increase during annealing at different elevated temperatures up to 140 °C does not show significant differences. Dry soy protein prepared by compression molding has a high elastic modulus of 1 to

2 GPa in the temperature range from –40 to 140 °C. The rigid nature of dry soy protein aggregates is therefore suitable as a reinforcement phase in rubber composites. A very significant reinforcement effect was observed from the significant increase of shear elastic modulus, which increased approximately 2.5 decades as the soy protein loading was increased to 40%. A comparison is made with rubber composites prepared from an aqueous dispersion of carbon black and the result indicates dry protein composites have higher elastic moduli at the same weight fractions of filler. The analysis with cluster–cluster aggregation model indicates a stronger bonding between protein particles can explain its reinforcement effect when compared to carbon black. The current test results indicate considerable promise of using renewable soy protein in certain rubber composites and applications for structural reinforcement.

#### Acknowledgements

The author thanks Dr C. J. Carriere for the valuable comments on the manuscript, A. J. Thomas for the rheological instruments, J. H. Salch for Fourier transform infrared spectroscopy and Dr A. R. Thompson for scanning electron microscopy.

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